

Effect of Doping on Nano Cadmium-Selenide (CdSe) - Assessment Through UV-VIS Spectroscopy



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(Received January 2011; accepted 23 March 2011)

Abstract

Cadmium Selenide (CdSe) has been synthesized in nanocrystalline form by wet chemical synthesis and then CdSe/Polythiophene nanocomposite has been prepared. The characteristics of nanocrystalline CdSe and nanocomposite CdSe/Polythiophene has been studied by UV-VIS (Ultraviolet-Visible) Spectroscopy. Reduction in band gap energy is observed on addition of polymer polythiophene with CdSe nanocrystal.

Keywords: Nanocrystal

Resumen

Se ha sintetizado seleniuro de Cadmio (CdSe) en forma nanocrystalina por síntesis química húmeda y luego han sido preparados CdSe/nanocompuestos de politiofeno. Las características del CdSe nanocrystalino y del nanocompuesto CdSe/politiofeno han sido estudiadas mediante espectroscopia UV-VIS (Ultravioleta-visible). Se observa una reducción en la banda de energía prohibida en adición de polímero politiofeno con con nanocrystalos de CdSe.

Palabras Clave: Nanocrystalos

PACS: 81.05.-t, 01.40.-d

ISSN 1870-9095

I. INTRODUCTION

There have always been demands from technology for the development and discovery of new materials with tailor-made properties. The most well known example of this is the 'electronics' technology, which has a continuous demand for the miniaturization of its components. Moreover today we have even smaller computers like the laptops, the palm held, and the ones in the cell phones, etc. This has become possible simply because of the state of art of miniaturization. The components used in electronic devices have gone through successive changes – from the vacuum tubes to semiconductor devices to integrated circuits to VLSI's. Nowadays a chip of one centimetre square area can contain as many as 10,000 devices. As a consequence of this miniaturization not only have the machines become smaller but there has also been a large saving in power consumption, resulting in the reduction in their cost. Gordon Moore, a computer scientist made the observation in 1965 that the number of devices placed on a chip was going to double every 18 to 24 months. His observation has not been violated till today; consequently his observation has come to be called the "Moore's law" as shown in the Fig. 1. However, if this process of miniaturization continues, soon we will come to a stage

when the electrical connectivity between the devices has to be replaced by optical connectivity.

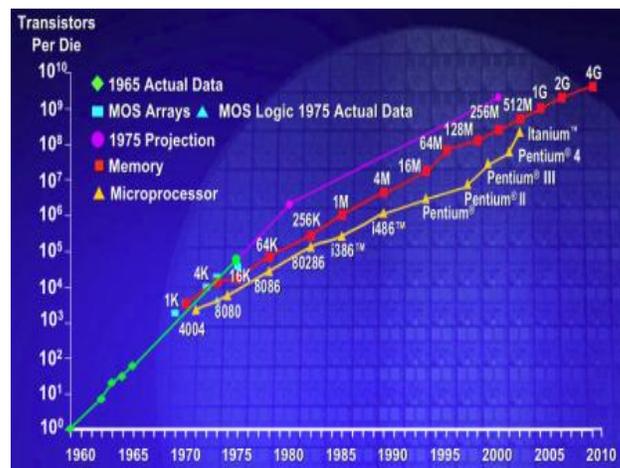


FIGURE 1. Moore's law.(Plot of CPU transistor counts against dates of introduction. Note the logarithmic scale; the fitted line corresponds to exponential growth, with transistor count doubling every two years.)

This will require the use of optoelectronic materials. Consequently, drastic changes in the computer industry will be called for. At present this technology is mainly based on the material silicon. Unfortunately silicon, which is a semiconductor with a small band gap, is not a light emitter and as such cannot be used for optical communication. The solution will be to find a new material that will be compatible with the requirements of the new technology. This in turn demands for the change of base of the industry, which will be rather expensive alternatively, silicon can be modified in some way such that its optical properties get suitably changed and it can be used for optical communication. One way to change the properties of a material is to reduce its size. On reducing the size of bulk silicon to nanometre scale, its band gap increases. Furthermore it can change over to a direct band gap material. These are the requirements for a semiconductor to emit visible light. Thus nanometre-sized silicon can find use as an optoelectronic device; hence will retain its place in the industry.

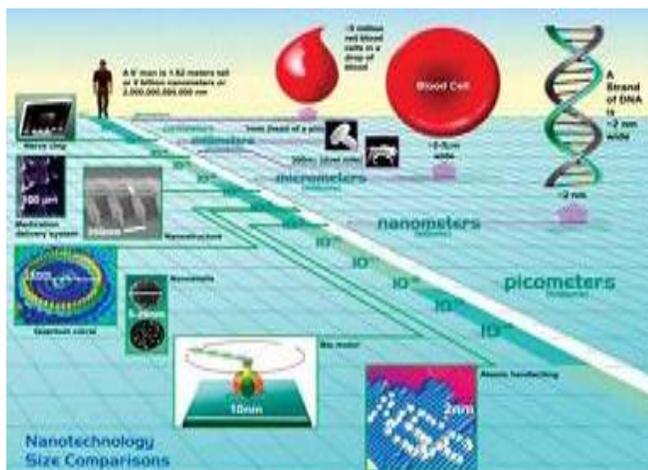


FIGURE 2. Nanotechnology size comparison.

The question then is: What are nanoparticles and why do the properties of materials change when one gets down to this size? Bulk materials have sizes ranging from microns to millimetres and above. The change in properties with reduction in size can be crudely illustrated with the simple example of a piece of chalk. One can write on a blackboard with a piece of chalk. This is so because the chalk is white, and as we write tiny pieces of the chalk material are removed due to friction and stick to the blackboard. If we break the piece of chalk into two, we can still write with any of the two pieces. However, if we continue to break the pieces, a limit will be reached when the piece will not be visible, and then it will not write on the blackboard any more. Thus below a critical size the piece of chalk loses its capability to write on the blackboard. As compared to bulk material a nanoparticle is one the size of which varies from a few nanometres (nm) to about 100nm. Needless to say that $1\text{nm} = 10^{-9}\text{m}$. Let us put this length in its proper perspective

by comparing it with the size of an atom. We study about atoms and are more familiar with atomic sizes, which are a few Angstroms (Å), with $1\text{Å} = 10^{-10}\text{m}$, which means $1\text{nm} = 10\text{Å}$. Therefore, to fix our ideas on sizes, it may be mentioned that three to four atoms on a line will amount to a nanometre. Even though we deal with atoms, we cannot see them. Therefore, it may be of further help in visualizing the size by considering our familiarity with a needle. One nanometre is a millionth part of the size of the tip of a needle. One nanometre is a millionth part of the size of the tip of a needle. A spherical particle with a diameter of 3nm contains as many as 900 atoms. The Energy band diagram of nanocrystalline cadmium selenide (CdSe) and bulk material. As shown in the Fig. 3.

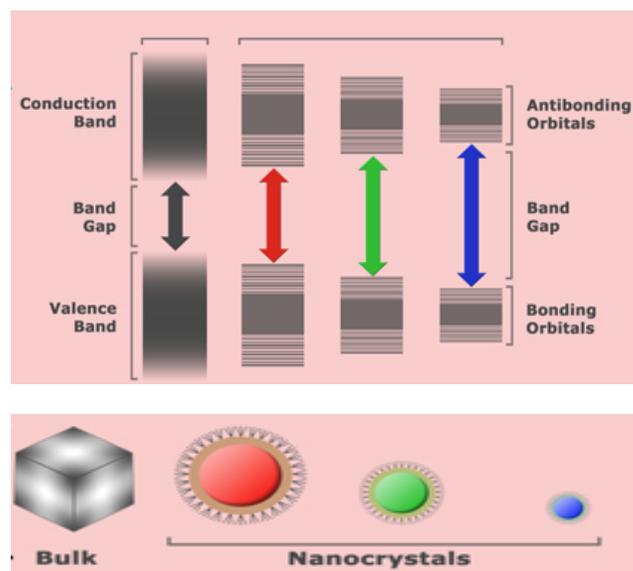


FIGURE 3. Energy band diagram of nanocrystalline CdSe and bulk materials.

For either of the abovementioned phenomena to occur the semiconductor must be of ‘direct band gap’ type, which is a requirement arising from momentum conservation in the process of light emission. Besides, for the emission of visible light of different wavelengths the band gap must have energy appropriate to the corresponding wavelength. This in turn requires that it should be possible to tune the band gap of the semiconductor. The commonly used semiconductor silicon is an ‘indirect band gap’ material with the magnitude of the gap rather small compared to the energy of light in the visible range. Hence it is not a light emitter. In contrast cadmium sulphide (CdS) and cadmium selenide (CdSe) are ‘wide band gap’ semiconductors. Hence these are more appropriate for light emission provided their band gaps can be tuned for emission of a particular colour of light. CdSe fulfills this requirement when prepared in the nanoform. When CdSe nanoparticles prepared in different sizes are suspended in a liquid and white light is shone on the test tubes containing these suspensions, each test tube emits light of a different colour

depending on the size of the nanoparticle suspended in it as shown in the Fig. 4. This clearly indicates that the band gap of CdSe changes depending on the size of the nanoparticle; in fact, the smaller the size the larger is the band gap of the material.



FIGURE 4. Fluorescence in different-sized CdSe quantum-dots.

In view of the resemble properties exhibited by CdSe nanocrystal and CdSe quantum dot we have undertaken the study of addition of polymer 'polythiophene' with CdSe and studied whether there is any change of band gap energy with the addition of polymer.

II. CADMIUM SELENIDE (CdSe)

Cadmium selenide is also a solid hexagonal or cubic crystal. It is a direct band gap n-type semiconducting material with a band gap of 1.74eV at 300K. Its molecular weight is 191.37g/mol where Cd is 58.74% and Se is 41.26%. Its appearance is dark red colour [1].

CdSe in the bulk form is not very interesting. The most interesting form of CdSe is nanoparticles. Much current research on CdSe has focused on nanoparticles. Researchers are concentrating on developing controlled synthesis of CdSe nanoparticles. It has useful properties for optoelectronic devices, laser diodes, nanosensing, biomedical imaging and high efficiency solar cells. The structure of CdSe is shown in Fig. 5.

A. Polythiophene

Polythiophenes are one of the most valuable types of conducting polymers that may be easily modified to afford a variety of useful electrical and physical properties such as solubility, electrical conductivity, mobility and others.

Polythiophenes are the polymerization of thiophenes (a sulphur heterocycle) i.e. a linear chain of thiophene monomers. This is shown in the Fig. 6. It possesses lower band gap and better electronic properties. It may give rise also some very useful properties such as increased ionization potential and stability [2, 3].



FIGURE 5. Cadmium selenide.

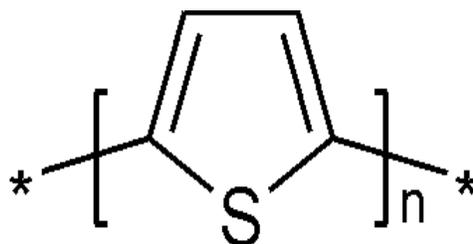


FIGURE 6. The monomer repeat unit of unsubstituted polythiophene.

B. Experimental

The experiment has been done in Centre for Materials For Electronics Technology (C-MET), Pune and Raman Research Institute, Bangalore.

C. Synthesis of Nanocrystalline CdSe: (Wet Chemical Synthesis).

In this procedure, first 0.4M Se metal powders were dissolved in 0.4M sodium sulphite solution. The solution was carried out at 60°C under stirring for 4-5 hours. Then the undissolved particles were filtered out after the solution cooled to the room temperature. That solution was sodium selenosulphate used as a selenium source. Second, in 35ml of distilled water and 15ml of isopropanol, 0.1M of cadmium sulphate solution was prepared. The prepared sodium selenosulphate solution was added drop wise to the stirred cadmium sulphate solution. After one hour, the products of dichromate coloured precipitates were collected and then washed with distilled water followed by absolute ethanol. The products were dried in a vacuum oven at 70°C for 6 hours. Finally the powders of nanocrystalline CdSe were collected [4, 5].

D. Synthesis of Polythiophene (PTH): (Oxidative Polymerization of Thiophene).

Here 0.1M of thiophene was dissolved in 25ml of acetonitrile or methanol (non-aqueous media) with 1ml of CTAB as surfactant. Then 0.3M of lithium perchlorate was

added as a supporting electrolyte to increase the bath conductivity and also added 0.1M of ferric chloride as an oxidant to the above stirred solution. Again stirred the above mixture for 2 hours and kept several hours for polymerization. Then the products of black coloured precipitates were collected. These products were washed thoroughly with acetonitrile to remove any residual ferric chloride. These products were dried in a vacuum oven at 70°C for 10 hours to get powder form of polythiophene [3, 6].

E. Synthesis of CdSe / PTh Nanocomposite

Here first Se metal powders were dissolved in 0.4M sodium sulphite solution at 60°C under stirring for 4-5 hours and then the undissolved particles were filtered out after the solution cooled to the room temperature. That solution was sodium selenosulphate used as a selenium ion source. Second, 50ml of methanol, 45ml of distilled water and 5ml of CTAB stock solution were added together and then divided into two equal volumes. 0.1M of thiophene, 0.3M of lithium perchlorate and 0.1M of ferric chloride solutions were prepared in one part. Again 0.1M of cadmium nitrate and the above prepared sodium selenosulphate solutions were prepared in another part. These solutions were mixed slowly under stirring for 1 hour and irradiated 20 KHZ frequency for 1 hour in an ultrasonic bath. The products of blackish-brown coloured precipitates were collected and then washed thoroughly with absolute ethanol. The final products were dried in a vacuum oven at 70°C for 10 hours. Finally CdSe/polythiophene nanocomposite powders were collected [4].

F. Deposition of Nanocomposite Thin Films: Electrodeposition

The nanocomposite thin films were galvanostatically deposited on copper substrates. Here 25ml of n-hexane, 25ml of distilled water and 1ml of CTAB were added together and divided into two equal parts. For CdSe/polythiophene film, 0.1M of sodium selenite was added instead of sodium thiosulphate. These solutions were added together slowly and applied 1.2-1.5 mA current for electrodeposition. After 75 minutes a brown coloured uniform film deposited on the copper substrate. Here copper substrate was connected to the cathode and graphite electrode was used as anode [7, 8].

III. RESULT AND DISCUSSION

A. UV-VISIBLE Spectrometer

We have used the Lambda 35UV- Visible Spectrometer which is a versatile spectrometer operating in the ultraviolet and visible spectral ranges. Lambda UV-Visible spectrometer is scanning double beam spectrometer uses two light sources, a deuterium lamp for ultraviolet light and a halogen lamp for visible light as shown in the Fig. 7. The

mirror M1 is raised to permit radiation from the lamps to strike source mirror M2. The radiation from the source lamp is reflected from source mirror M2 through an optical filter to pass through a slit and hits a diffraction grating (monochromator) which can be rotated allowing a specific (single) wavelength to be selected. Appropriate optical filter on a filter wheel assembly located on the beam path to pre filter the radiation before it enters the monochromator.

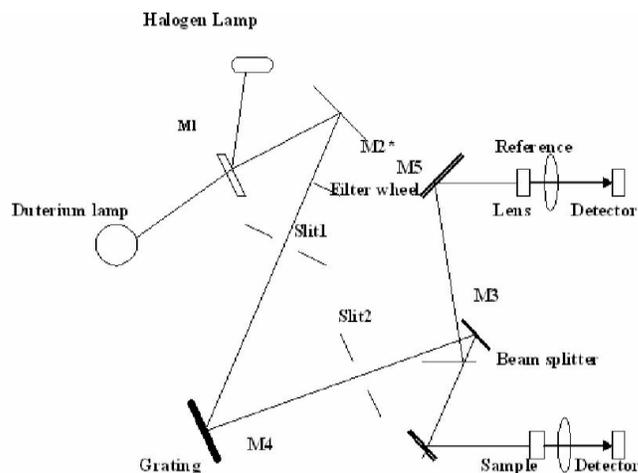


FIGURE 7. Block Diagram of UV-Visible Spectrometer.

The radiation is dispersed at the monochromator to produce a spectrum. The rotational position of the grating effectively selects a segment of the spectrum, reflecting this segment through exit the slit 2 to mirror M3. This slits provide a spectral selectable band pass of 0.5, 1, 2 or 4nm. From the mirror M3 the radiation is reflected onto a beam splitter, which allows 50% of the radiation to pass onto the plane mirror M4, and reflects 50% of the radiation onto the plane mirror M5. Mirror M4 focuses the radiation beam to the sample cell. The beam then passes through a convex lens onto the photodiode detector. Mirror M5 focuses the radiation beam in to reference cell. The beam then passes through a convex lens onto the photodiode detector. The advantage of double-beam operation is the better stability and allows reference to be measured and corrected in real time and fast scanning is done. The grating monochromator used here is a holographic concave grating with 1053 lines /mm in the center. Photodiodes are used as detectors. The optical path length in the sample compartment is 121mm. This spectrometer can be operated in an ambient operating temperature of 15°C to 35°C and humidity range of 20% to

80% without condensation. The power requirements to operate this spectrometer are about 100V to 240VAC, frequency of 50/60Hz.

B. Ultraviolet-Visible (UV-VIS) Spectroscopy Results:

Fig. 8 shows the UV-VIS reflectance spectrum of nanocrystalline CdSe prepared by wet chemical synthesis.

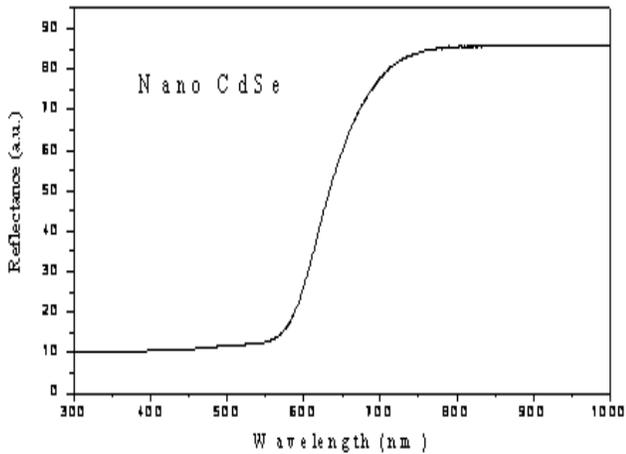


FIGURE 8. UV-VIS spectrum of nanocrystalline CdSe.

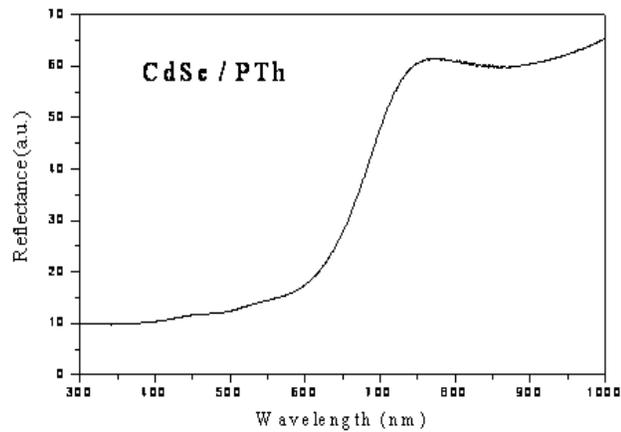


FIGURE 9. UV-VIS spectrum of CdSe/Polythiophene nanocomposite.

Using this absorption band edge value, the band gap energy was calculated as $E_g = 1.76\text{eV}$. Fig. 9 shows the UV-VIS reflectance spectrum of CdSe/polythiophene nanocomposite. From the spectrum the absorption band edge of CdSe/polythiophene nanocomposite is around 750nm, which corresponds to the band gap energy $E_g = 1.65\text{eV}$. From the Figs. 10 and 11 one can see that the absorption bands are decreases by the addition of polymer polythiophene.

Based on this reflectance spectrum, the band edge of nanocrystalline CdSe is around 705nm.

IV. CONCLUSION

In conclusion, it is summarized that CdSe/polythiophene nanocomposites are successfully synthesized in room temperature and pressure. CdSe nanocrystals are of uniform size and nearly monodispersion, which are disordered and mixed with polythiophene matrix. From UV-VIS spectroscopy, the band gap energy of nanocrystalline CdSe is 1.76eV where as CdSe/polythiophene nanocomposites is 1.65eV respectively which shows that CdSe/Polythiophene nanocomposite is more efficient material than CdSe nanocrystal. We acknowledge Prof S. N. Behera by borrowing some of his material letters from his article published in monthly news letter of vigyan prasar (2047).

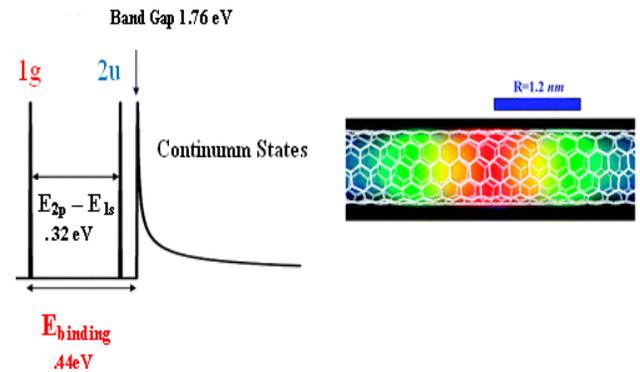


FIGURE 10. Energy band diagram of CdSe nanocrystal.

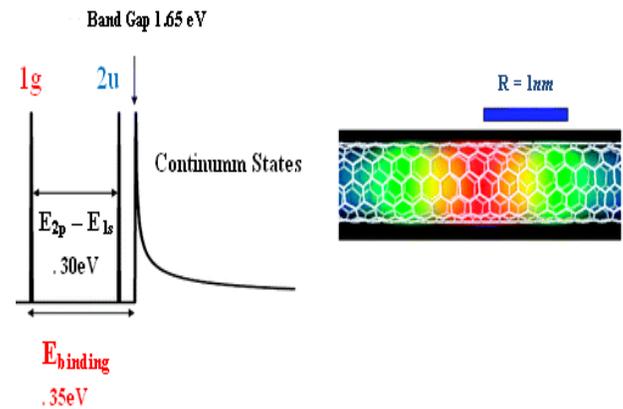


FIGURE 11. Band gap of Nanocomposite CdSe/Polythiophene.

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